PATENT SPECIFICATION (11) 1 445 071

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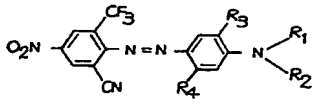
(72) Inventors GERHARD BUTTNER, ERICH KLAUS and KLAUS LEVERENZ

(54) AZO DYESTUFFS

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to azo dyestuffs of the formula



(I)

wherein

R_1 represents hydrogen, C_1-C_4-alkyl, C_1-C_4-chloroalkyl, C_1-C_4-hydroxyalkyl or C_1-C_2-alkoxy-C_1-C_4-alkyl,

R_2 represents R_1, cyclohexyl, benzyl, phenylethyl or phenyl,

R_3 represents hydrogen, methyl or methoxy and

R_4 represents hydrogen, methyl, methoxy, ethoxy, Cl, $NHSO_2CH_3$ or $NHSO_2C_2H_5$

and to their preparation and use.

Preferred dyestuffs of the formula I are those wherein

R_1 to R_3 have the stated meaning and

R_4 represents Q,

wherein

Q denotes H, methyl, methoxy, ethoxy or chlorine.

Dyestuffs of the formula I which are very particularly preferred are those wherein

R_3 and Q have the stated meaning and

R_1 represents hydrogen or C_1-C_3-alkyl and

R_2 represents C_1-C_3-alkyl.

[illegible] for example combining diazotised

PATENTS ACT 1949

SPECIFICATION NO 1445071

The following corrections were allowed under Section 76 on 20 September 1976

Page 1, Heading (72) Inventors, *for* ERICH KLAUS *read* ERICH KLAUKE

THE PATENT OFFICE
14 October 1976

Bas 31177/6

SEE CORRECTION SLIP ATTACHED

wherein

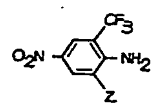
R_1 to R_4 have the abovementioned meaning and

Z represents Cl, Br or I,

the substituent Z is replaced by a cyano group.

This replacement reaction is in itself known (compare British Patent Specification 1,125,683 = French Patent Specification 1,511,932, as well as German Patent Application P 23 10 745.1) and is effected by reaction of III with metal cyanides, preferably CuCN, in organic aprotic solvents or in an aqueous medium to which a nitrogen base has been added, at elevated temperatures, preferably at 60 to 120°C. Preparative details are to be found in the literature references mentioned.

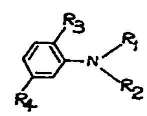
Compounds of the formula III are in part known (compare US Patent Specifications 2,491,481, 2,590,092 and 2,618,631) and are obtainable in a manner which is in itself known by diazotisation of anilines of the formula



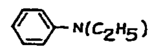
(IV)

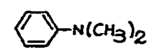
and coupling to appropriate coupling components.

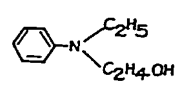
Suitable coupling components of the formula

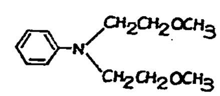


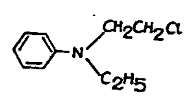
are:

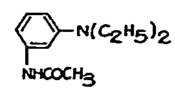


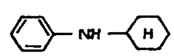


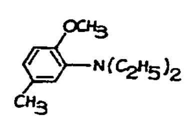


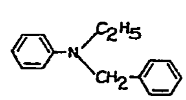


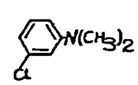


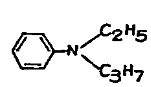


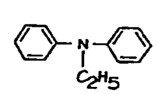


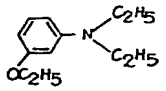
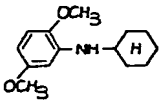
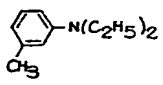
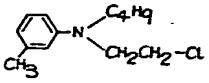
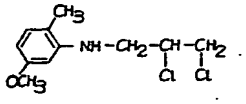
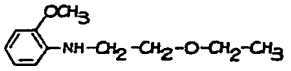










The new dyestuffs are outstandingly suitable for dyeing and/or printing synthetic fibre materials by conventional methods, but especially by the so-called transfer printing process.

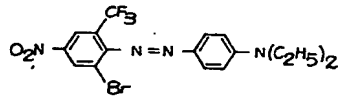
The transfer printing process is generally known and has been described, for example, in French Patent Specifications 1,223,330 and 1,334,829. The dyestuffs, for example in the form of so-called printing inks, such as are described, for example, in French Patent Specification 1,573,698, or in the form of pastes, are applied to so-called auxiliary carriers (paper, other cellulosic materials, such as cotton or cellophane, metal foils and the like, such as are known, for example, from French Patent Specification 1,575,069). These printing inks are dyestuff solutions, also containing synthetic resin, in suitable organic solvents, such as benzene, toluene, xylene, chlorobenzene, chloroform, dichloroethane, trichloroethylene, perchlorethylene, ethanol, iso-propanol, benzyl alcohol, cyclohexanone, ethyl acetate or their mixtures. The printing inks and printing pastes can, however, also be made up on an aqueous basis and are thus dispersions of the dyestuffs in water, which in addition contain customary dispersing agents and thickeners (compare French Patent Specification 1,223,330) and US Patent Specification 3,647,503). The printing inks can be printed in accordance with the customary printing processes (relief printing, gravure printing, offset printing, film printing and screen printing).

Suitable substrates for transfer printing with dyestuffs of the formula I are textile materials which consist wholly or predominantly of polyesters, such as polyethylene glycol terephthalate, poly-1,4-bis-hydroxymethylcyclohexane terephthalate or cellulose triacetate and cellulose 2½-acetate or of polyamides or polyacrylonitrile, but also non-textile plastics articles, such as films, tapes or blocks of commercially available polymerisation or polycondensation plastics.

The prints obtained are distinguished by very good fastness properties, especially by high fastness to light.

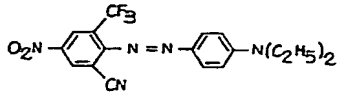
Example 1.

16.5 g of 2-amino-3-bromo-4-nitro-trifluoromethyl-benzene are introduced into a mixture of 32 ml of 96% strength sulphuric acid and 9.8 ml of nitrosylfulphuric acid (2.45 ml of nitrosylsulphuric acid correspond to 1 g of Na NO_2) whilst stirring at 0 to 5°C and the mixture is stirred for a further 3 hours at this temperature. 8.9 g of N,N-diethylaniline are dissolved in 250 ml of ice water with addition of 6 ml of 48% strength sulphuric acid. After addition of 0.5 g of aminosulphonic acid, the above diazotisation mixture is allowed to run in slowly whilst stirring and at the same time the temperature is kept at between 0 and 5°C by addition of ice. The coupling is complete after a short time. the resulting dyestuff of the formula



is filtered off, washed with water until neutral and dried. 19.8 g of this product, with the addition of 3.6 ml of pyridine, are reacted in 50 ml of dimethylformamide

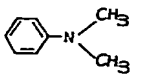
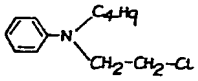
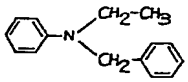
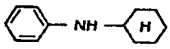
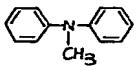
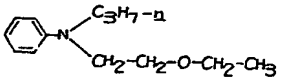
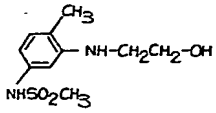
with 3.9 g of CuCN for 1 hour at 80 to 90°C, whilst stirring. After cooling to room temperature, the reaction products are precipitated with water, filtered off and introduced into a solution of 8 g of iron-(III) chloride in 100 ml of 10% strength hydrochloric acid to remove Cu-(I) salts. After stirring overnight, the dyestuff of the formula



is filtered off and washed with water until neutral. After drying, a dark powder is obtained, which dyes polyethylene terephthalate fibres in clear, blue-violet shades of very good fastness to light.

If, in this example, the N,N-diethylaniline is replaced by the coupling components indicated in the Table which follows, dyestuffs with similar properties are obtained, which dye polyester fibres in the stated shades:

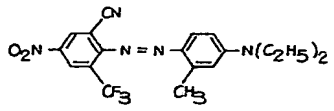
TABLE

Coupling component	Colour shade
	blue-violet
	violet
	violet
	violet
	violet
	blue-violet
	blue-violet

Example 2.

11.7 g of 2-amino-3-cyano-5-nitro-trifluoromethyl-benzene are introduced at maximally 0°C into a mixture of 65 ml of 96% strength sulphuric acid and 35 ml of 85% strength orthophosphoric acid and 8.6 ml of nitrosylsulphuric acid (2.45 ml correspond to 1 g of Na NO_2) are slowly added dropwise at −5 to −2°C, whilst stirring. The mixture is stirred for a further 5 hours at maximally 0°C.

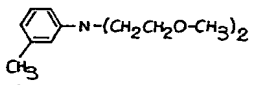
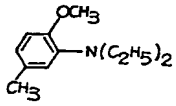
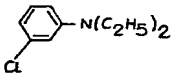
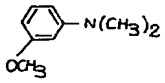
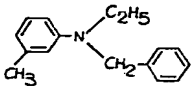
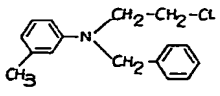
8.3 g of 3-(N,N-diethylamino)-toluene are dissolved, with addition of 5 ml of 48% strength sulphuric acid, in 150 ml of ice water. After adding 0.5 g of aminosulphonic acid, the diazotisation mixture is slowly added dropwise and at the same time the temperature is kept below 0°C by dropping ice into the mixture. The coupling is complete after a short time. The dyestuff which has precipitated, of the formula



is filtered, washed until neutral and dried. The dark powder dyes polyester fibres in light-fast, clear, blue shades.

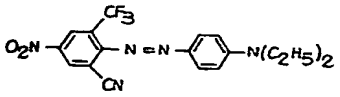
If, in Example 2, the coupling component is replaced by the compounds indicated in the table which follows, dyestuffs which dye polyester fibres in the stated shades are obtained:

TABLE

Coupling component	Colour shade
	blue
	blue
	violet
	blue
	blue
	blue-violet

Example 3.

A) 75 g of the dyestuff of the formula



50 g of an anionic dispersing agent, for example of a lignin-sulphonate or of a condensation product of naphthalenesulphonic acid and formaldehyde, and 100 ml of water are mixed and converted to a finely divided form by grinding in a ball mill for 10 hours. The dispersion thus obtained, which contains approx. 30% of crude colourant, is stable on storage.

B) the aqueous dispersion obtained according to A) can be converted to a printing paste as follows:

50 to 200 g are worked into a paste with 400 g of a 10% strength carob bean flour ether thickener and 550 to 400 ml of water.

C) A paper is printed with this printing paste by the gravure printing process. If this paper is pressed against a textile of polyester fibres for 15 to 60 seconds at 200°C, a clear, deep, somewhat blue-violet print with good fastness properties is obtained.

Comparably good results are achieved with the dyestuffs tabulated above.

Example 4.

A) 40 to 50 g of the dyestuff used in Example 3 are worked into a paste with 5 to 10 g of an emulsifier mixture of ethoxylated nonylphenol (4 to 12 mols of ethylene oxide) in water. 10 g of ethylcellulose N4 ("Hercules" Powder) and 30 to 40 parts of a maleate resin which has been prepared by condensation of colophony with maleic acid are added. The mixture is kneaded for approx. 2 hours at 80 to 100°C and then ground on one of the customary mills. A finely granular dyestuff powder is obtained.

B) 200 g of the dyestuff powders obtained according to A) are added, whilst stirring, to a mixture of 730 g of ethanol, 50 g of ethylene glycol and 20 g of ethylcellulose N22 ("Hercules" Powder).

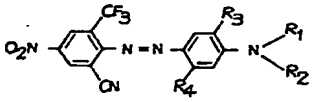
C) Papers can be gravure-printed with the printing ink thus obtained. Cellulose triacetate textiles, for example knitted fabrics, can be printed by means of these printed papers in the transfer process, and strong blue-violet prints are obtained.

Comparably good results are achieved with the dyestuffs tabulated above.

The word "Hercules" used herein is a Trade Mark.

WHAT WE CLAIM IS:—

1. An azo dyestuff of the general formula



(I)

in which R_1 stands for a hydrogen atom or a C_1-C_4 alkyl, C_1-C_4 chloroalkyl, C_1-C_4 hydroxyalkyl or C_1-C_2 alkoxy-C_1-C_4 alkyl group,

R_2 has the same meaning as R_1 or stands for a cyclohexyl, benzyl, phenylethyl or phenyl group,

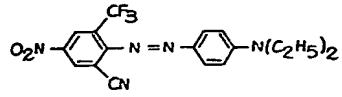
R_3 stands for a hydrogen atom or a methyl or methoxy group and

R_4 stands for a hydrogen or chlorine atom or a methyl, methoxy, ethoxy, $NHSO_2CH_3$ or $NHSO_2C_2H_5$ group.

2. An azo dyestuff according to claim 1, in which R_4 stands for a hydrogen or chlorine atom or a methyl, methoxy or ethoxy group.

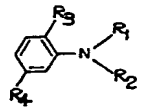
3. An azo dyestuff according to claim 2, in which R_1 stands for a hydrogen atom or a C_1-C_3 alkyl group, R_2 stands for a C_1-C_3 alkyl group and R_3 has the same meaning as in claim 1.

4. The azo dyestuff according to claim 1 of the formula



5. An azo dyestuff according to claim 1 as hereinbefore specifically identified.

6. A process for the production of an azo dyestuff as claimed in claim 1, in which 2-cyano-4-nitro-6-trifluoromethylaniline is diazotised and coupled with a coupling component of the general formula

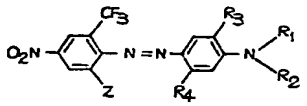


(II)

in which R_1, R_2, R_3 and R_4 have the same meanings as in claim 1.

7. A process according to claim 6, in which the coupling component of formula (II) is any of those hereinbefore specifically mentioned.

8. A process for the production of an azo dyestuff as claimed in claim 1, in which, in an azo dyestuff of the general formula



(III)

in which R_1, R_2, R_3 and R_4 have the same meanings as in claim 1 and Z stands for a chlorine, bromine or iodine atom, the substituent Z is replaced by a cyano group.

9. A process for the production of an azo dyestuff as claimed in claim 1, when carried out substantially as described in Example 1 or 2.

10. An azo dyestuff as claimed in claim 1, when produced by the process of any of claims 6 to 9.

11. A process for dyeing a synthetic fibre material comprising treating the material with an azo dyestuff as claimed in any of claims 1 to 5 and 10.

12. A process according to claim 11, in which the dyeing is a transfer printing process.

13. A process according to claim 12, when carried out substantially as described in claim 11 or 12.

14. A synthetic fibre material when dyed by the process of any of claims 11 to 13.

15. A printing ink or printing paste for use in transfer printing comprising an azo dyestuff as claimed in any of claims 1 to 5 and 10.

16. An auxiliary carrier for transfer printing when printed with a printing ink or printing paste as claimed in claim 15.

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